THE W WILL BE NO "SON OF SUPERGAS"

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1.0   WHAT DO WE WANT IN A HALON REPLACEMENT?

Over the past few years much research effort has been expended in the search for a "drop-in" replacement for Halon 1301, particularly for applications where weight and space considerations predominate such **as** aviation. Sometimes the impression is given that what is sought is a material with all the chemical, physical, toxicological, and fire suppression properties of Halon 1301, so that no system change whatsoever is necessary, but without any adverse environmental properties (ozone depletion or global warming effects). This paper attempts to give **a** scientific critique of the search for "drop-in" replacements.

An agent must satisfy several inter-related criteria to be considered as a viable "drop-in" replacement for halon. The complex inter-relationship between the selection criteria is illustrated in Figure 1. These criteria include the following:

- Acceptable fire suppression performance. The material needs to have the same or similar performance as Halon 1301 in weight and container volume terms, and preferably similar safety margins.

- Acceptable toxicity. Again the various applications (whether normally occupied or otherwise) may have different criteria [1].

- Acceptable environmental characteristics. Currently a physically acting agent with zero ODP is acceptable, but to incorporate a chemically active species (in practice, the element bromine) the molecule needs to tropospherically degradable. Routes to tropospheric degradability are discussed in the following section.

- Acceptable volatility. It is necessary to define temperature limits for the various applications. For example, aerospace and military applications may demand total-flooding performance at temperatures as low as −60 "C, whereas industrial applications sometimes specify temperatures only **as** low as 0 **"C.** This leads to the likely scenario that different applications could utilise different replacement agents. Factors affecting volatility are discussed in Section 3.

2.0   TROPOSPHERIC DEGRADABILITY

2.1   Basic Mechanisms
There are several basic mechanisms for the breakdown of organic molecules released into the atmosphere [2, 3].

START → Define lifetime for tropodegradability → k_{OH} limits

Structural groups that could work → Molecular weight & volatility considerations

% halogen in molecule

Flammability? — No → Extinguishing concentration at a given temperature

Yes

Density
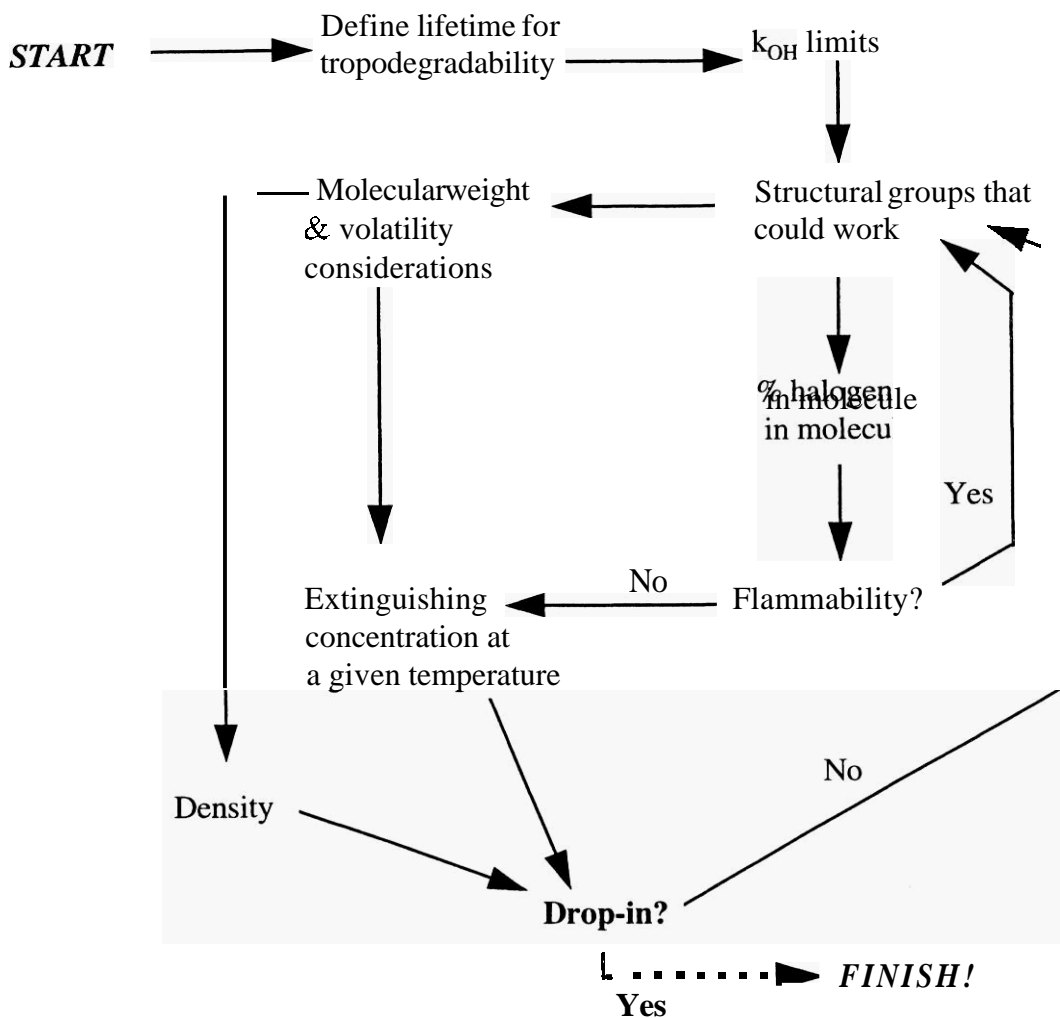
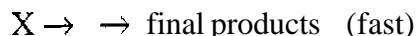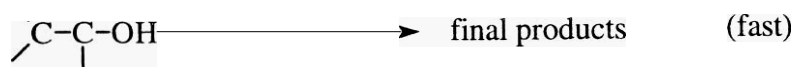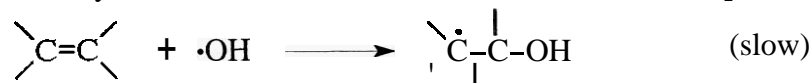Drop-in?

No

Drop-in?

⋯⋯▶ *FINISH!*

Yes

Figure 1. Agent Selection Strategy.

- **Reaction with •OH radicals: This** is the principal tropospheric degradation mechanism for most organic molecules. The most common reaction is that of hydrogen atom abstraction.

$$X-H + OH \rightarrow X + H_2O \quad \text{(slow)}$$

$$X \rightarrow \quad \rightarrow \text{final products} \quad \text{(fast)}$$

The rate of the whole process is controlled by the rate of the first reaction, the hydrogen abstraction reaction. The radical X then breaks down very rapidly to the final products such as CO_2, H_2O, HF, HBr, etc., which are washed **out** of the atmosphere in rain. Clearly the molecule must possess an abstractable hydrogen atom for this reaction to occur. There is also another possibility, namely addition of the •OH radical to a double bond, e.g.,

$$\text{C=C} \quad + \cdot OH \longrightarrow \text{C-C-OH} \quad \text{(slow)}$$

$$\text{C-C-OH} \longrightarrow \text{final products} \quad \text{(fast)}$$

- **Hydrolysis:** Providing the molecule contains hydrolytically unstable bonds. An example of this might be PBr_3 where reaction with water vapour generates HBr and phosphorous-containing acids, both **of** which are then rapidly washed out of the atmosphere in rain.

- **Photolysis:** Providing the molecule contains a UV-absorbing chromophore, such as a double bond, $C=C$ or $C=O$, or a weak single bond such as C—I, then degradation in the troposphere may occur readily.

- **Reaction with 0 3 and N03:** These two species contribute only a very minor part of the tropospheric degradation mechanisms in comparison with the •OH reaction route and will not be considered further.

2.2   Reaction with Hydroxyl Radicals

For most molecules released into the atmosphere, degradation occurs through reaction with •OH radicals. The global average •OH radical concentration* is around 6.5 x 10^5 molecules cm^{-3} [2] and bearing in mind that 1 year = 3.156 x 10^7s, then the lifetime of a molecule in the atmosphere,[†] T, is given by [3],

$$\tau = \frac{4.9 \times 10^{-14}}{\overset{\cdot}{k}_{OH}} \text{ years}$$

where k_{OH} is the rate constant **for** reaction of •OH with the molecule.

This relationship is shown in Figure 2. Note that some earlier texts (e.g., [3]) quote the •OH radical concentration **as** 1 **x** 10^6 molecule cm^{-3}, thus there may be some variation in the precise form of the above equation. Note also that to remove essentially all of a compound from the atmosphere requires three lifetimes. Thus for most organic molecules, i.e., those not photolysed or hydrolysed, the estimation of the atmospheric lifetime comes down, in the end, to either the measurement [4-7] or estimation of the rate constant k_{OH}. The latter can be done by various structure activity relationships [**3,** 8].

2.3   Importance of Atmospheric Lifetime

The atmospheric lifetime plays a key role in determining the global warming potential (GWP) of an agent, the intrinsic power of a given molecule to cause global warming. This is a relative scale with the GWP of the reference molecule (usually CO_2) being arbitrarily assigned a value of 1.0,

$$GWP \text{ (for } \mathbf{X}) = \frac{\text{calculated radiative forcing for unit emission rate of } \mathbf{X}}{\text{calculated radiative forcing for unit emission rate } \mathbf{of} \, CO_2}$$

Factors used in the calculation are (i) the lifetime of the molecule in the atmosphere and (ii) the position and intensities of the IR absorption bands of the molecule relative to the re-radiation energy spectrum from the earth's surface [9-11]. The calculation is typically performed over a 100-yr time horizon. Figure 3 shows how GWP and lifetime vary for some hydrofluorocarbons

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* There is considerable variation with season, latitude, and altitude.
[†] The lifetime of a molecule in the troposphere, τ, is defined as the time taken for its concentration to be reduced to 1/e of its starting value.

Figure 2: Relationship of k_{OH} and Calculated Atmospheric Lifetime
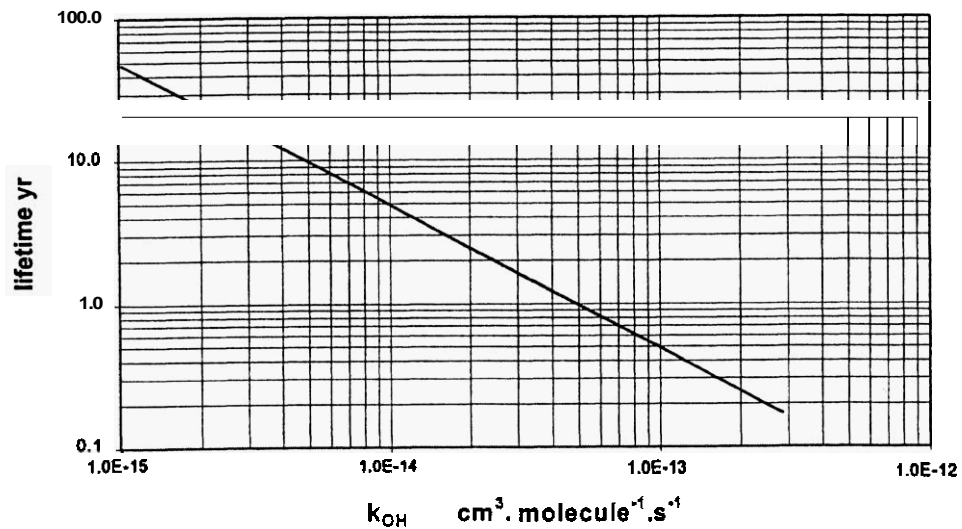

Figure 3: Relationship of Atmospheric Lifetime and GWP
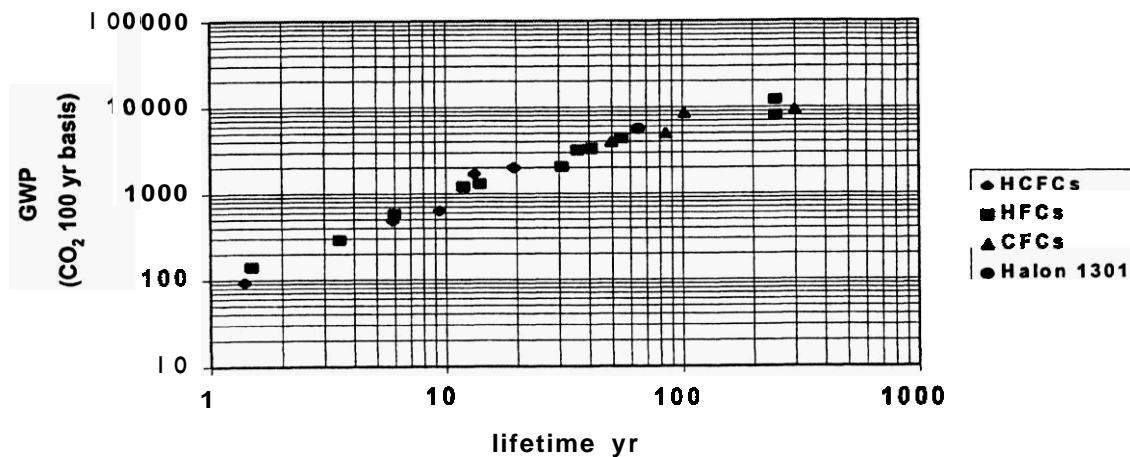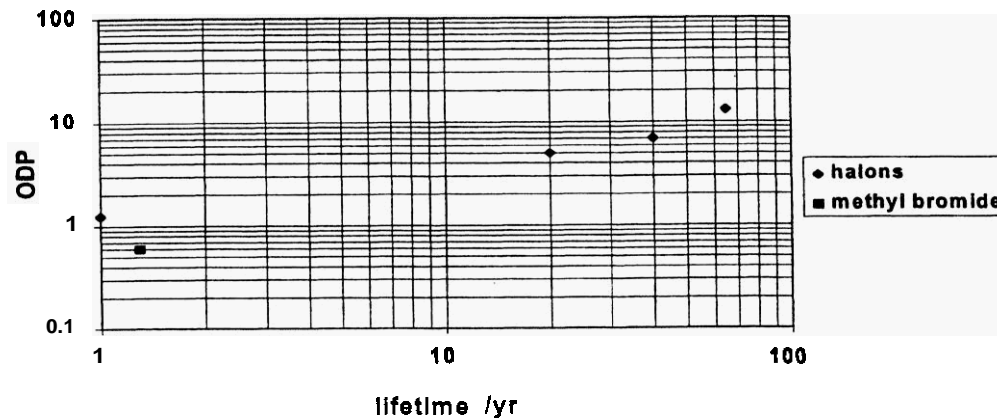

Figure 4: Relationship of Atmospheric Lifetime and ODP

(HFC) and hydrochloro-fluorocarbons (HCFC) [12]. **As** can be seen, because most organic molecules will have some absorptions, of probably broadly similar intensities, in the key 5-15µm spectral region, atmospheric lifetime is the principal feature differentiating between different molecules, at least to a first order of approximation. Similar considerations affect ozone depletion and ODP (Figure 4).

2.4   Structural Moieties Reacting with •OH

None of the above mechanisms, and particularly that of reaction with •OH, can operate with the halons. **As** a result, they have relatively long lifetimes in the atmosphere (τ for Halon 1301 is ⁻ 65 yrs); their only destruction mechanism is photolysis in the stratosphere by short wavelength solar UV radiation.

Thus, to reduce the atmospheric lifetime, by making use of the •OH radical reactions of the troposphere, it is necessary to modify the halon molecule by the incorporation of at least one structural moiety capable of reacting with •OH. Clearly, we want to retain as much as possible of the halon molecule, and in particular, the bromine atom, in order to give a chemical fire suppression effect [13]. In addition, one or more of the fluorine atoms have to be retained to avoid the material being flammable. So we are considering molecules of the type $Br\text{-}CF_2\text{-}X$, where, X is a structural feature of the molecule, which guarantees a short lifetime.

Table 1 lists some typical groups and gives the k_{OH} values as estimated by the method published by NIST [3, 8], from which approximate lifetimes can be estimated for the CF_2BrX molecule. Other more complicated substituents are possible, with several different types of abstractable hydrogen atoms.

Note that with the exception of the very simplest substitutions of F by H, or of F by CH_3, one side effect is to increase the molecular weight. All such substitutions will also lead to an increase in the dipole moment of the molecule and an increase the intermolecular attractions. The consequences of these effects on other properties of the agent will be considered in the following section.

Table 1. Possible Substituents for Tropodegradability.

X (in CF_2BrX)	Estimated k_{OH} 10^{-12} cm^3 molecule-' s^{-1}	Relative k_{OH}	Estimated Lifetime yr	Increase in Molecular Weight for Substitution F → X
F	not applicable	not applicable	65	0
H	5.38E-03	1	9.1	-18
CH_3	3.6E-03	0.67	14	-4
CH_2F	2.07E-03	0.39	24	14
CHF_2	4.48E-04	0.08	109	32
OCH_3	1.19	220	0.041	12
$COCH_3$	0.109	20	0.45	24
$COOCH_3$	0.187	35	0.26	40
$CH=CH_2$	6.6	1200	0.007	8
C_6H_5	0.48	89	0.10	58

3.0   VOLATILITY ISSUES

3.1   Introduction
During the last two years several groups have investigated candidate agents with tropospherically degradable properties. To date no viable replacement agents that satisfy all of the criteria listed in Section 1.0 have been identified. One of the main pitfalls is that the incorporation of the functional groups such as those listed in Table 1 invariably leads to a large decrease in the agent volatility, rendering the molecule unsuitable for total-flooding applications. This section examines the underlying physical chemistry that determines the volatility of a given molecule and explains why this should be the case.

3.2   Factors that Influence Boiling Point
The boiling point **of** a molecule is governed by various intermolecular attractions. These include (in increasing order of strength) van der Waals attractions, dipole-dipole attractions and hydrogen bonding. All molecules possess van der Waals attractions that are related to the polarizability of the molecule, and in the absence of any dipole or hydrogen bonding, van der Waals forces increase with molecular weight, giving rise to the commonly encountered trend of increasing boiling point with increasing molecular weight within **a** homologous series (i.e., little variance in dipole moments **or** hydrogen bonding).

After van der Waals attractions, dipole-dipole interactions are considered next. Polar molecules typically have higher boiling points than nonpolar molecules of equivalent molecular weight. Molecules that can undergo hydrogen bonding have the highest boiling points. Water is a good example of a molecule with extensive hydrogen bonding, having a boiling point of 100°C, despite a molecular weight of only 18!

Having considered the various intermolecular forces, it is necessary to consider the effect these forces have on possible elements in our candidate molecules. In this regard the element fluorine is unique. Compounds containing fluorine exhibit **low** polarizability, low dipole moments, and very low intermolecular interactions in general [14]. This is illustrated in Table **2** below, where the properties of various chlorofluoromethanes are examined [15-17].

Table 2. Effect of Dipole Moment and Permitivity on Boiling Point.

Molecule	Molecular Weight.	Relative Permitivity*	Dipole Moment (Debye)	Boiling Point (°C)	Increase in Boiling Point from F → H Substitution (°C)
$CHCl_3$	119.5	4.80	1.01	+61	
$CFCl_3$	137.5	2.24	0.45	+24	37
$CHFCl_2$	103	5.34	1.29	+9	
CF_2Cl_2	121	2.13	0.51	-30	39
CHF_2Cl	86.5	6.15	1.42	-41	
γCF_3Cl	104.5	2.3	0.5	-81	40

* Relative Permitivity **(or** dielectric constant) is closely related to the polarizability of the molecule.

In each case, the substitution of a fluorine by a hydrogen atom leads to an **increase** in the boiling point of approximately 40 **K,** due to the effect of intermolecular forces, despite a reduction of 18 in the molecular weight.

Another example of the extremely low intermolecular forces associated with fluorine atoms is the fact that perfluoroalkanes have boiling points only marginally higher than the noble gas of the same molecular weight [IS]. Figures 5–7 illustrate these points.

Figure 5 shows the boiling points of the first 10 perfluorocarbons and the corresponding hydrocarbons plotted against molecular weight. Figure 6 shows the perfluorocarbons and hydrocarbons compared on the basis of the number of carbon atoms in the molecule. Figure 7 shows the boiling points of the first 4 perfluorocarbons and hydrofluorocarbons also plotted against number of carbon atoms.

Of course none of these molecules contains bromine, but the volatility trends of replacing a fluorine atom with something even as simple as a hydrogen atom are evident. Therefore, any replacement of a fluorine atom by any other atom or functional group will lead to an increase in intermolecular attraction, hence an increase in boiling point.

The functional groups outlined in Table 1 that offer the highest values of k_{OH} and hence the shortest atmospheric lifetime are, not surprisingly, those that would impart large dipole moments and add significantly to the molecular weight, reiterating the point made above.

4.0   EXAMPLES OF STRATEGIES EMPLOYED SO FAR

4.1   Replacement of F by H

Replacement a fluorine atom in CF_3Br, Halon 1301, by a hydrogen atom leads to CHF_2Br, bromodifluoromethane, otherwise known as FM100™, and launched as a fire suppressant by Great Lakes Chemical in 1990. This structural change in the molecule is the minimum conceivable that will yield tropodegradability, without losing the good fire suppression properties associated with bromine-induced chemical activity. In fact the heptane cup-burner minimum extinguishing concentration is 4.2 - 4.4 vol.%. However, there are certain problems with this structural change.

- In spite of a reduction in the molecular weight to 131 (compared with 149 for Halon 1301), the increased dipole moment and intermolecular forces (see above) leads to an increase in boiling point (from -58°C for CF_3Br to -15°C for CHF_2Br) and reduced volatility, as was seen in Table 2.

- The fluorine and bromine attached to the carbon atom of the C—H bond are very electronegative and withdraw electrons from the bond. Unfortunately, the •OH radical is electrophilic, and this means that the rate of reaction is relatively low (in comparison to hydrocarbons) (Table 1). This results in an atmospheric lifetime of around 7 years and an ODP value of around 1.1, which was too high for regulatory approval. Similar considerations apply to the compound put forward by ICI, 2-bromo-1,1,1,2-tetrafluoroethane, CF_3CHFBr, (HBFC-124B1).

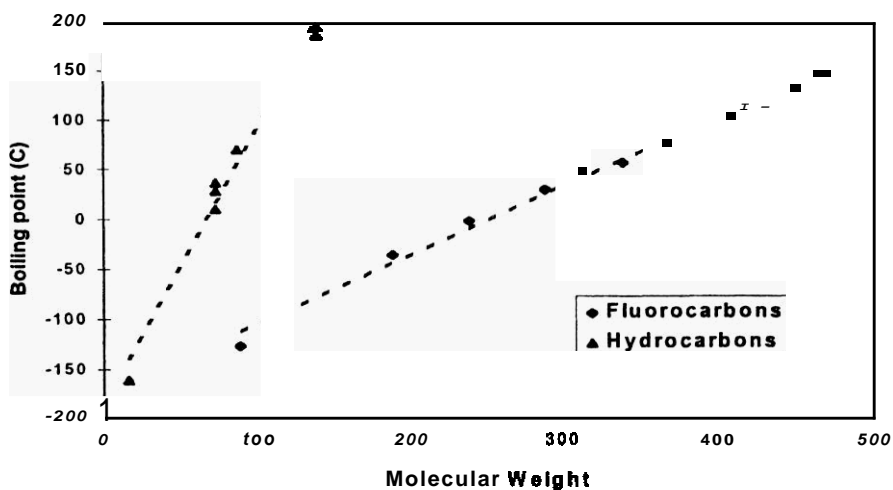**Figure 5: Comparison of Fluorocarbons with Hydrocarbons**

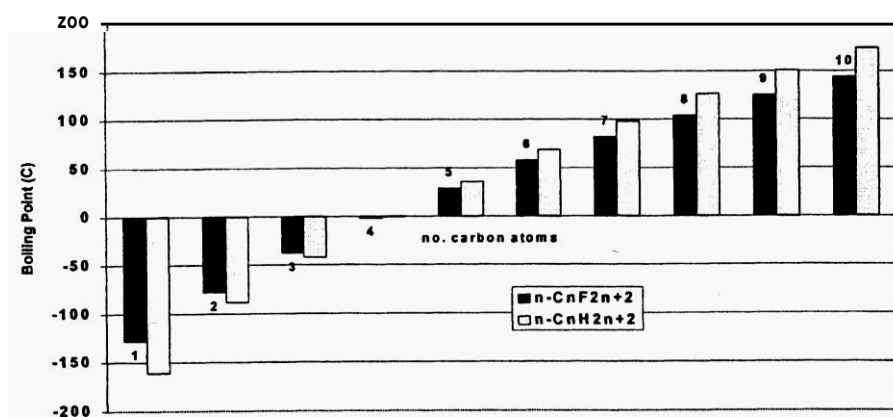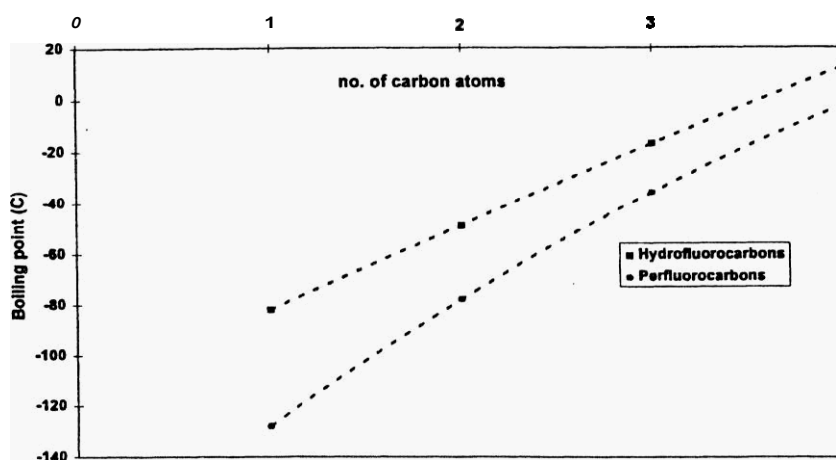**Figure 6 Boiling Points of n-Alkanes**

Figure 7: Comparison of Perfluorocarbons with Hydrofluorocarbons

4.2   Introduction of Methoxy and Other High kOH Substituents

An alternative strategy is to introduce substituents into the molecule that will yield as high a rate of reaction with *OH radicals as possible. A good example of such a substituent is the methoxy group, CH_3O- (Table 1). Kidde International have pursued this approach [19]. The compound studied was 2-bromo-I,1,2-trifluoro-1-methoxyethane, CH_3OCF_2CHFBr. The rationale for selecting this material was (i) that it was easily synthesised in the laboratory, (ii) the simpler compound CH_3OCF_2Br was more likely to be toxic by reason of a labile bromine atom, and (iii) it was not on the AAWG list of compounds for study [20-22]. Although the material is a reasonable fire suppressant and, because of the CH_3O- group, has an estimated atmospheric lifetime of 2 weeks to 2 months, it is not a drop-in agent because of its low volatility. The molecular weight has increased to 193, a 30% increase over Halon 1301, yet the boiling point is now $^-89°C$, an increase of over 140 K over that of Halon 1301, which emphasises the points discussed in Section 3 above.

Unsaturated groups, such as $CH_2=CH-$, have been considered as part of the AAWG programme [21]. Two candidates that went forward onto the short list are $CH2=CH-CF_2Br$ and $CH_2=CH-CF_2CH_2$ Br. The first one of these has a molecular weight of 157 (only a slight increase on the 149 of Halon 1301) yet the boiling point has increased from –59 "C to +40-42 °C for this substitution. Thus, again, the introduction of a group conferring short atmospheric lifetimes (in the case of the $CH_2=CH-$ agents just a few days) has resulted in a considerable loss of volatility, such that the material could not be considered a "drop-in" agent.

4.3   Non-in-Kind Alternatives

Various other strategies have been investigated that would lead to halon alternatives that are not based on substituted bromofluorocarbons:

- **phosphonitrilic halides:** compounds such as $P_3N_3F_6$ or $P_4N_4F_8$ have been investigated and found to have relatively high fire suppression performance as measured by the cup-burner concentration in vol.% [23]. However, because of their high molecular weight, these compounds are inefficient suppressants, in weight terms, and they also have low volatility. Thus, they are unlikely to **be** "drop-in" agents.

- **phosphorus tribromide:** this high boiling point liquid has been claimed as a high performance suppressant [24]. But with a boiling point approaching 180 "C, and with a freezing point above the lowest temperature specified for many applications, such an agent will never be a "drop-in" replacement for Halon 1301.

- **iron pentacarbonyl:** This material was first investigated more than 30 years ago [25] and again more recently [26, 27], and found to be a potent inhibitor of hydrocarbon flames at very low concentrations (although its suppression performance did not show the same degree of improvement over Halon 1301). Its high toxicity precludes its practical use as a fire suppressant, even if its physical properties do not. Nevertheless, it would, at first sight, suggest that iron chemistry should be a fruitful area of research for new dry chemicals. It is inconceivable that a gaseous "drop-in" halon replacement will arise, if only because the atomic weight of iron is 56, which does not leave much leeway for substituent groups before the molecular weight of Halon 1301 is exceeded.

5.0 CONCLUSIONS

The search for a "drop-in" halon replacement for total-flooding applications (as defined in 1.0) thus seems unlikely to be successful. Rather than waiting any longer, the halon users should take action now, and accept that "something has to give."

- **Compromise on volatility:** Use engineering means to deliver less volatile agents to the fire, e.g., with specially designed pipework and nozzles or using gas generators to enhance atomisation (for example, CH_2BrCl (bp 67 °C) was used in engine nacelle applications in the 1950s and early 1960s). This will probably mean increased system weight.

- **Compromise on performance:** Use agents such as the HFCs, as has been done in the general industrial sector, which also has system weight implications. This means that, for aviation applications, reducing emission of ozone depleting substances could lead to increased emission of the greenhouse gas, CO_2, through increased fuel consumption. Another way of compromising on performance, although less desirable, would be to reduce safety factors, where possible.

- **Compromise on toxicity:** Use an agent such as CF_3I, with the attendant problems of manufacture, filling, distribution, handling, recharge and recycling.

- **Compromise on tropodegradability, and thus GWP or ODP** Accept the use of an ozone depleting or global warming agent and protect the environment by other means, such as a stringent control on emissions during the product cycle. The same considerations could even apply to continued use of recycled Halon 1301.

6.0 REFERENCES

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